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Abstract

Elastic properties of carbon nanotubes (CNT), boron nitride nanotubes (BNNT), double stranded DNA (dsDNA), paranemic-juxtapose crossover (PX-JX) DNA and dendrimer bound DNA are discussed in this thesis. Structural phase transitions of nucleic acids induced by external force, carbon nanotubes and graphene substrate are also studied extensively. Electrostatic interactions have a strong effect on the elastic properties of BNNTs due to large partial atomic charges on boron and nitrogen atoms. We have computed Young's modulus (Y) and shear modulus (G) of BNNT and CNT as a function of the nanotube radius and partial atomic charges on boron and nitrogen atoms using molecular mechanics calculation. Our calculation shows that Young's modulus of BNNTs increases with increase in magnitude of the partial atomic charges on B and N atoms and can be larger than the Young's modulus of CNTs of same radius. Shear modulus, on the other hand depends weakly on the magnitude of partial atomic charges and is always less than the shear modulus of the CNT. The values obtained for Young's modulus and shear modulus are in excellent agreement with the available experimental results.

We also study the elasticity of dsDNA using equilibrium fluctuation methods as well as non-equilibrium stretching simulations. The results obtained from both methods quantitatively agree with each other. The end-to-end length distribution $P(\rho)$ and angle distribution $P(\theta)$ of the dsDNA has a Gaussian form which gives stretch modulus (γ_1) to be 708 pN and persistence length (L_p) to be 42 nm, respectively. When dsDNA is stretched along its helix axis, it undergoes a large conformational change and elongates about 1.7 times its initial contour length at a critical force. Applying a force perpendicular to the DNA helix axis, dsDNA gets unzipped and separated into two single-stranded DNA (ssDNA). DNA unzipping is a fundamental process in DNA replication. As the force at one end of the DNA is increased the DNA starts melting above a critical force depending on the pulling direction. The critical force f_m, at which dsDNA melts completely decreases as the temperature of the system is increased. The melting force in the case of unzipping is smaller compared to the melting force when the dsDNA is pulled along the helical axis. In the case of melting through unzipping, the double-strand separation has jumps which correspond to the different energy minima arising due to sequence of different base-pairs.

Similar force-extension curve has also been observed when crossover DNA molecules are stretched along the helix axis. In the presence of mono-valent Na^+ counterions, we find that the stretch modulus (γ_1) of the paranemic crossover (PX) and its topoisomer juxtapose (JX) DNA structure is significantly higher (~ 30 %) compared to normal B-DNA of the same sequence and length. When the DNA motif is surrounded by a solvent of divalent Mg^{2+} counterions, we find an enhanced rigidity compared to in Na^+ environment due to the electrostatic screening effects arising from the divalent nature of Mg^{2+} counterions. This is the first direct determination of the mechanical strength of these crossover motifs which can be useful for the design of suitable DNA motifs for DNA based nanostructures and nanomechanical devices with improved structural rigidity. Negatively charged DNA can be compacted by positively charged dendrimer and the de-

gree of compaction is a delicate balance between the strength of the electrostatic interaction and the elasticity of DNA. When the dsDNA is compacted by dendrimer, the stretch modulus, γ_1 and persistence length, L_p decreases dramatically due to backbone charge neutralization of dsDNA by dendrimer.

We also study the effect of CNT and graphene substrate on the elastic as well as adsorption properties of small interfering RNA (siRNA) and dsDNA. Our results show that siRNA strongly binds to CNT and graphene surface via unzipping its base-pairs and the propensity of unzipping increases with the increase in the diameter of the CNTs and is maximum on graphene. The unzipping and subsequent wrapping events are initiated and driven by van der Waals interactions between the aromatic rings of siRNA nucleobases and the CNT/graphene surface. However, dsDNA of the same sequence undergoes much less unzipping and wrapping on the CNT/graphene due to smaller interaction energy of thymidine of dsDNA with the CNT/graphene compared to that of uridine of siRNA. Unzipping probability distributions fitted to single exponential function give unzipping time (τ) of the order of few nanoseconds which decrease exponentially with temperature. From the temperature variation of unzipping time we estimate the free energy barrier to unzipping. We have also investigated the binding of siRNA to CNT by translocating siRNA inside CNT and find that siRNA spontaneously translocates inside CNT of various diameters and chiralities. Free energy profiles show that siRNA gains free energy while translocating inside CNT and the barrier for siRNA exit from CNT ranges from 40 to 110 kcal/mol depending on CNT chirality and salt concentration. The translocation time τ decreases with the increase of CNT diameter having a critical diameter of 24 Å for the translocation. After the optimal binding of siRNA to CNT/graphene, the complex is very stable which can serve as siRNA delivery agent for biomedical applications. Since siRNA has to undergo unwinding process in the presence of RNA-induced silencing complex, our proposed delivery mechanism by single wall CNT possesses potential advantages in achieving RNA interference (RNAi).